AN EXPLORATORY STUDY ON THE OXYGENATION OF ISOPROPYL ETHER

A THESIS

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CHAPTER I

INTRODUCTION

It was suggested that an organic peroxide, if reacted with an ether in the presence of a suitable catalyst such as chloroacetic acid, salts of cobalt, iron or manganese, would oxidize the ether to form a new peroxide. This newly formed peroxide would decompose to give the original ether and molecular oxygen. The oxygen which is liberated from the peroxide would react with a mole of the original ether to give a free radical which initiates a free radical chain reaction. As a result of this reaction there should be an increase in the internal pressure. Equations for the expected reactions are:

$$R\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}R + R'OR' \xrightarrow{H^{+}} R\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}R + R'OOR'$$

$$R'OOR' \xrightarrow{Co^{++}} R'OR' + \tfrac{1}{2}\,O_2$$

$$\tfrac{1}{2}\,O_2 + R'OR' \xrightarrow{H^{+}} 2\,R'O\cdot$$

The study was made on the effect of benzoyl peroxide on isopropyl ether. Controlled reactions were carried out and results were recorded and analyzed for further action.

As a result of preliminary experimentation it was recognized that the expected reaction did not occur immediately but rather, an absorption of a gaseous substance was realized which was indicated by a decrease in

pressure. However, closer observation of several runs revealed an initial increase in pressure followed invariably by a decrease in pressure. The increase varied proportionally with the concentration of reactants and presence of solvent. When cumene was used as the solvent there was no observable increase whatsoever.

Through further experimentation it was found that the observed reaction was really involving the oxygen and the isopropyl ether. It has been the authors purpose to gather data which would aid in identifying products formed in this system which would lead to an explanation for the increase and ultimate decrease in pressure. The rate of the reaction would also aid in proposing mechanisms for the reactions. The experimental problem, essentially then, was to do an exploratory study on what was later recognized as an ultimate absorption of oxygen by isopropyl ether. Because this study is one of a general nature, it will serve as supporting information toward additional investigation of similar systems.

CHAPTER II

REVIEW OF THE LITERATURE

A search was made for any previous studies related to the described work contained in this paper. A summary of the findings of several investigators will be given here.

Ivanov, Savinova and Mikhailova[1] report that isopropyl ether, being oxidized at a temperature of 50 degrees with a stream of oxygen, yielded three types of peroxides; hydrogen peroxide, a small amount of low-boiling organic peroxide and principally, a higher-boiling organic peroxide. The main product of the initial autoxidation was shown to be a dihydroperoxide. Its structure is represented by $HOOC(CH_3)_2OC(CH_3)_2OOH$. A higher sufficient amount of "light peroxide" was isolated from a very large run to establish its physical constants. It is apparently a monohydroperoxide of the structure $(CH_3)_2CHOC(CH_3)_2OOH$. The monohydroperoxide is formed in small yields, however, and appears to be an intermediate which is rapidly converted to the dihydroperoxide, since the latter is the main isolatable peroxide product. It was shown that ultraviolet radiation accelerates the autoxidation of isopropyl ether and does not change the course of the reactions.

In Georges Radulesco's article,[2] it is pointed out that purified

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[1] K. I. Ivanov, V. K. Savinova, and E. G. Mikhailova, J. Gen. Chem. (U.S.S.R.), 16, 65-70 (1946).

[2] Georges Radulesco, Ann. Combustible Liquids, 13, 1071-82 (1938).

isopropyl ether absorbs no oxygen in six months in the dark. Radulesco used a 500-watt lamp to irradiate his reaction. He reports that after an induction period of 10 hours, photoxidation of the thermostated reaction begins. Three volumes of oxygen per volume of liquid were absorbed in 800 hours. Dilution with gasoline up to 90 per cent lowers the rate in proportion to its concentration. No effect was observed upon varying the oxygen pressure. Radulesco's reaction products consisted of $(CH_3)_2CO$, H_2O, traces of peroxide, acid and gum.

Glen A. Russell,[3] in an effort to explain the initial reaction between oxygen and ethyl linoleate, states that:

> Originally, it was believed that a thermal reaction had been observed since the rate of oxidation was observed to be proportional to the amount of oxygen absorbed. Such a relationship is consistent with the occurrence of a chain process involving the following steps:
>
> Initiation: $2\ ROOH \longrightarrow RO\cdot + ROO\cdot + H_2O$
>
> Propagation: $R\cdot + O_2 \longrightarrow ROO\cdot$
>
> $ROO\cdot + RH \longrightarrow ROOH + R\cdot$
>
> Termination: $2\ ROO\cdot \longrightarrow$ Nonradical products
>
> The bimolecular nature of the initiation by hydroperoxide was independently verified. Extrapolation of the straight line in figure 1 gives a definite intercept which was originally interpreted as being due to a thermal reaction between oxygen and the olefin. However, experiments at extremely low hydroperoxide concentrations indicated that the rate of oxidations actually followed the dotted line. This behavior is consistent with an initiation process that is bimolecular in hydroperoxide at high hydroperoxide concentrations but unimolecular at low concentrations. Because of the curvature of the dotted line, it is impossible to state whether a direct thermal reaction between ethyl linoleate and oxygen can be detected.

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[3] Glen A. Russell, J. Chem. Ed., 36, 111-18 (March, 1959).

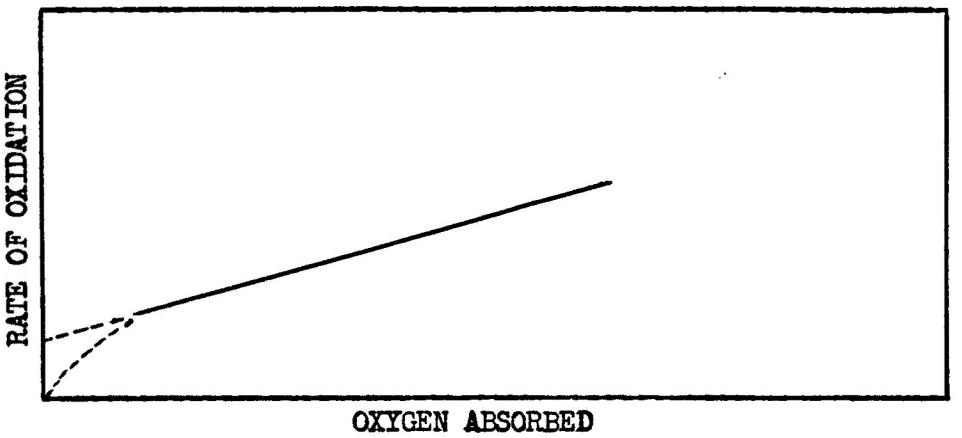

Figure 1. Relationship between the amount of oxygen absorbed and the rate of oxidation of ethyl linoleate

Molodovskii and Neiman[4] made a study on the oxidation of isopropyl ether in the liquid phase. A decrease in pressure was detected during this reaction. It was noted in their paper that after 10 hours of reacting isopropyl ether with oxygen the rate, $-\frac{dp}{dt}$, reached a maximum value. The concentrations of the peroxides (c) formed, which were determined iodometrically and polarographically, increased for 10 hours and then remained constant. The rate was reported as being $10^{-7}(.1 + .4 \times 10^{5}c)p^{3}$mm/hr. The original pressure was 575 mm.

It was pointed out by Bolland and Gee[5] in their publication on the kinetics of oxidation of unconjugated olefins that the peroxide content of the reaction was confirmed by the use of ferric thiocyanate, colorimetric determination and the iodine method of Dastur and Len. Bolland indicated his belief that the reaction was one of autoxidation catalyzed by peroxide. He also encountered great difficulty in obtaining reproducible values for the initial rate of oxidation. Bolland assumed a

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[4]V. A. Molodovskii and M. B. Neiman, J. Phys. Chem., 23, 30-6 (1949).
[5]J. L. Bolland and G. Gee, Trans. Faraday Soc., 42, 236 (1946).

decomposition of peroxides. He stated that traces of free acids were present which apparently accelerated the rate of peroxide decomposition. His proposed mechanism for the reaction:

$$RH + O_2 \longrightarrow \text{free radicals}$$

$$RH + O_2 \longrightarrow R\bullet + HOO\bullet$$

$$R\bullet + O_2 \longrightarrow ROO\bullet$$

$$ROO\bullet + RH \longrightarrow R\bullet$$

$$ROO\bullet + RH \longrightarrow ROOH + R\bullet$$

Waters[6] made oxygenation studies originally on tetralin and later expanded his investigations to include many organic compounds, one of which was isopropyl ether. It was indicated that the oxygen uptake by the tetralin was regarded as a diagnostic test for the presence of free radicals in this article. The uptake was a regular phenomenon. In this system chromic acid was used as an autoxidation chain starter. It abstracts a hydrogen atom from the tetralin, forms a free radical and immediately combines with oxygen. It was noted that oxygen was absorbed by the reacting system only while reduction of the acid was in process. When this reaction was studied using isopropyl ether the reactivity was slight with some sign of oxygen uptake.

Peroxides were detected as the products of the oxidation of ethers in the gaseous phase as recorded by T. A. Eastwood and Cyril Hinshelwood.[7] Among the ethers studied was ethyl ether.

The production of peroxides by the oxidation of hydrocarbons was

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[6]William A. Waters, J. Chem. Soc., 1151 (1946).

[7]T. A. Eastwood and Cyril Hinshelwood, J. Chem. Soc., 733-8 (1952).

supported again by Bolland[8] where he states that the reaction occurs by the way of a radical chain mechanism. The initiating free radicals may be formed in various ways, i.e., photochemically, or by the decomposition of radical producing catalysts such as benzoyl peroxide. The hydroperoxide that is formed also acts as a source for free radicals which gives rise to autoxidation.

On the study of the oxidation of benzyl ether,[9] it was reported that the principal primary product is most probably the hydroperoxide, $C_6H_5CH_2OCH(OOH)C_6H_5$. It was found that the oxidation rate was proportional to the intensity of absorbed light, independent of the concentration of oxygen and proportional to the concentration of the ether between 0° C and 30° C and oxygen pressure of 250 to 650 mm of mercury. The process was carried out by radical induced reactions.

Upon studying the gaseous system, ethyl ether and oxygen,[10] at 53° C and constant volume the findings indicate that there was an initial induction period of little pressure change. The pressure then increased rapidly and leveled off. During the first phase of the reaction the concentration of acetic acid and the hydroperoxide, AcOOH, reached a maximum and then decreased. There was a constant decrease in the concentration of ethyl alcohol. There were traces of hydrogen peroxide and organic hydroperoxides. Acetic acid and smaller amounts of methyl alcohol and formaldehyde formed in the second phase. These products were reported

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[8] J. L. Bolland, Quart Reviews, 3, 1 (1949).

[9] Louis Debiais, Michel Neclause and Maurice Letort, J. Chim. Phys., 56, 41-53 (1959).

[10] D. J. Waddington, Proc. Roy. Soc., A252, 260-72 (1959).

as resulting from a radical chain mechanism following an initial attack of oxygen on the alpha carbon atom of ethyl ether.

Noller[11] indicates that ethers are very easily oxidized. This is readily manifested by the frequency with which violent explosions have been reported when residues from the distillation of ether have been heated beyond the boiling point of the ether. This same type of explosion occurs if the residue is agitated by pulverizing or grinding in any way.

It has been proposed many times that upon oxidizing ethyl ether the initial product is the hydroperoxide.

$$CH_3CH_2)_2O + O_2 \longrightarrow CH_3\underset{\underset{O\text{-}OH}{|}}{C}HOCH_2CH_3$$

The presence of hydrogen peroxide as an autoxidation product has been reported by many investigators. Ethyl vinyl ether has been postulated as possibly arising from the hydroperoxide (I) and alpha hydroxyethyl peroxide which presumably arises from a series of reactions (II).

(I) $$CH_3\underset{\underset{O\text{-}OH}{|}}{C}HOCH_2CH_3 \longrightarrow CH_2{=}CHOCH_2CH_3 + H_2O_2$$

(II) $$CH_3\underset{\underset{O\text{-}OH}{|}}{C}HOCH_2CH_3 + H_2O \longrightarrow CH_3\underset{\underset{O\text{-}OH}{|}}{C}HOH + C_2H_5OH$$

$$CH_3\underset{\underset{O\text{-}OH}{|}}{C}HOH \rightleftharpoons CH_3CHO + H_2O_2$$

$$CH_3\underset{\underset{OH}{|}}{C}H\text{-}O\text{-}OH + OCHCH_3 \longrightarrow CH_3\underset{\underset{OH}{|}}{C}H\text{-}O\text{-}O\text{-}\underset{\underset{OH}{|}}{C}HCH_3$$

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[11] Carl R. Noller, "Chemistry of Organic Compounds," W. B. Saunders Company, Philadelphia, Penn., 1958, p. 884.

Tobolsky and Mesrobian,[12] in their book summarize these findings and conclusions. They state that ethers are very susceptible to autoxidation and the formation of peroxidic products. These workers report that knowledge concerning the autoxidation mechanism and the structure of the peroxides formed is extremely limited since the identification of hydroperoxides formed by this method is still in its infancy. However, as indicated by other workers, it is pointed out in the discussion that the initial product of isopropyl ether is a hydroperoxide which converts to the dihydroperoxide:

$$CH(CH_3)_2OCH(CH_3)_2 + O_2 \longrightarrow HOOC(CH_3)_2OCH(CH_3)_2$$

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[12] Arthur V. Tobolsky and Robert B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N.Y., 1954, pp. 16-17.

CHAPTER III

PRELIMINARY EXPERIMENTATION

Chemicals and Apparatus Used. - The chemicals necessary to carry out this phase of the work were 2-(1-methylethoxy)-propane (isopropyl ether), 2-methyl-2-propanol (t-butyl alcohol), chloroethanoic acid (chloroacetic acid), benzoyl peroxide, cobalt II chloride and molecular oxygen.

The apparatus used for preliminary exploration consisted of 500 ml round bottom flasks and latex rubber diaphragms.

Experimental Procedure. - One thousand milliliters of t-butyl alcohol were carefully distilled in an all glass distillation apparatus. Care was taken not to use any rubber materials throughout the experiments with exception of the latex rubber diaphragms because of their peroxide content. The first fraction of distillate was discarded and the portion which distilled at a constant 80° C was collected and stored in a clean, dry, dark bottle.

A volume of 500 ml of isopropyl ether was washed with 10% ferrous sulfate until no further color change occurred, washed with distilled water, dried with two portions of sodium sulfate, and stored in a clean, dark bottle over forty mesh calcium chloride for approximately sixteen hours to allow for complete removal of moisture. The dried isopropyl ether was distilled and the portion which distilled at a constant 67° C was collected and stored in a clean, dark bottle.

After having completed preliminary preparations, three control systems were set up. Round bottom flasks (500 ml) were used for these systems. Flask I was used as a blank run. It contained 20 ml of isopropyl ether and 200 ml of t-butyl alcohol. Flask II contained 20 ml of isopropyl ether, 200 ml of t-butyl alcohol and 11 mg of cobalt II chloride. Twenty milliliters of isopropyl ether, 200 ml of t-butyl alcohol, 11 mg of cobalt II chloride and 11 mg of chloroacetic acid were introduced into flask III. Benzoyl peroxide (4.6 gm) was added to the three flasks.

Latex rubber diaphragms were securely fitted over the three reaction vessels to retain any gas that may be formed. The flasks were placed in a dark place and allowed to stand overnight, approximately 12 hours. Upon observance of the reaction vessels after this time lapse, no noticeable reaction had occurred. Twenty three and five tenths grams of cumene were added to each system to increase the solubility of benzoyl peroxide. The peroxide remained undissolved and no noticeable reaction occurred.

A second run was prepared and each system was set up as before with the exception of the use of t-butyl alcohol. This was left out of the systems. Cumene (200 ml) was used in each system as a solvent for benzoyl peroxide which dissolved almost completely upon agitating the flasks. Care was taken to add benzoyl peroxide to the flasks behind an explosion screen as a precautionary measure against a sudden and vigorous liberation of gas.

Upon standing overnight the reaction vessels were checked for changes. The benzoyl peroxide was completely dissolved but cobalt II chloride remained undissolved. There was a decrease in the internal

pressure in flasks I and II but little or no observable decrease in flask III. This pressure decrease was indicated by the fact that the diaphragms had been pulled into the reaction vessels. The change was more pronounced in flask I. Flask II showed about one third the change of flask I. These results were analyzed and equations for possible reactions were theorized:

$$(A) \quad O_2 + iPr)_2O \xrightarrow[\text{catalyst}]{Bz_2O_2} iPr)_2O_2$$

$$(B) \quad Bz_2O_2 + iPr)_2O \longrightarrow C_6H_5\overset{O}{\overset{\|}{C}}\text{-O-O-iPr} + \text{Bz-O-Bz}$$

Such an analysis warranted further investigation. Thus, to verify or disprove the proposed reactions, two other samples were prepared. The first reaction vessel contained 20 ml of isopropyl ether, 200 ml of cumene, 4.6 gm of benzoyl peroxide and was flushed with oxygen. The second flask contained equal amounts of the same chemicals but was flushed with nitrogen rather than oxygen.

After approximately five hours, the diaphragms had been completely pulled into the oxygen-flushed vessel but there was no change in the nitrogen-flushed vessel. These results indicated that oxygen was being absorbed by an unknown chemical reaction.

Other samples were prepared as indicated:

Flask I	200 ml cumene 20 ml isopropyl ether flushed with oxygen
Flask II	30 ml isopropyl ether flushed with oxygen
Flask III	30 ml cumene flushed with oxygen

The results were quite different from those of previous observations. Immediately there was a continuous inflation of the diaphragm which was fitted over the vessel containing 30 ml of isopropyl ether and was flushed with oxygen. No noticeable change occurred in the other two vessels.

To substantiate these results other samples were prepared:

Flask I	20 ml isopropyl ether 200 ml cumene 4-5 grains benzoyl peroxide flushed with oxygen
Flask II	10-15 drops isopropyl alcohol 40 ml isopropyl ether metallic sodium flushed with oxygen

Again there was a limited but continuous inflation of the diaphragm on the second flask. Upon checking the samples after approximately 3 hours time lapse, both diaphragms had been suctioned into the reaction vessels. When a mixture of 40 ml of isopropyl ether, cobalt II chloride and oxygen was swirled, again there was an inflation of the diaphragm. Inflation was also observed from a sample of 40 ml of isopropyl ether, chloroacetic acid and oxygen but it was much slower and was not of the magnitude of the first mixture.

CHAPTER IV

MAJOR WORK

Chemicals and Apparatus Used. - The chemicals required for major experimental work were isopropyl ether, molecular oxygen and cumene.

Apparatus of major importance to this phase of the work were an all glass manometric system, constant temperature bath, Cenco Vapor Phase Analyzer 70130 with a Servographic Recorder and the Perkin-Elmer 237B Grating Infrared Spectrophotometer.

Experimental Procedure. - Careful preparation was made for the proposed kinetic studies which would compose a portion of the general study. Because the most useful method for following gaseous reactions is manometric, an all glass pressure-determining apparatus with two side arms was constructed. All necessary calibrations were carefully made on the apparatus. The volume of the reaction vessel was 535.7 ml. The remaining portion of the apparatus was then measured. The volume was 154.2 ml. The total volume of the apparatus was 689.9 ml. A 3-ml magnetic stirrer was used for continuous stirring of the reaction mixture.

Each run was thermostated at or very near 25° C. Initial atmospheric pressures, original pressure reading of manometer, concentrations of all reactants and time were recorded. The concentration of the oxygen was calculated from the ideal gas law, i.e., $PV = nRT$:

$$n = \frac{(735/760 \text{ atm})(.6899 \text{ l})}{(.082 \text{ l-atm/deg-mole})(298 \text{ deg})} = .0274 \text{ mole}$$

.0274 mole/.6899 liter=.0397 mole/liter

This concentration of oxygen was used for each run. Various concentrations of isopropyl ether were used. In several of the runs 20% less than 1/3 of the concentration of oxygen was used which was .74256 gm. One hundred milliliters of cumene were used as solvent for the isopropyl ether and only 80 ml of this solution were used which reduced the amount of isopropyl ether to .5940 gm.

To assure the interaction of only those chemicals which should be involved in the reaction, the system was thoroughly cleaned, flamed under reduced pressure to facilitate the removal of moisture, flushed with dry air for approximately 30 minutes and completely evacuated and flushed with oxygen several times before the isopropyl ether and cumene (in cases where cumene was used) were added. These reactants were added through the funnel specially prepared to fit into the arm of the reaction vessel. Just before the ether was added, the oxygen-filled system was closed off completely. The manometer was equilibrated as the ether was added slowly to the system. The ether was never allowed to run below the stopcock on the arm of the reaction vessel so that no air would be allowed to enter. Stirring was started immediately and continued throughout the recording of pressure changes. Pressure readings were taken at both regular and irregular intervals.

It was observed that a decrease in pressure was always the result after a short induction period when cumene was used but invariably no noticeable increase.

In several systems 80 ml of isopropyl ether were used without cumene.

This was done in order to create a situation which would lend itself to a pseudo first order reaction if the reaction containing the cumene solvent possibly exhibited a first order in oxygen and first order in the ether. The table below will give recordings of the two different types of systems described above.

TABLE 1.--Recording of pressure changes for two runs

Run No. 1 - Cumene Solvent	
$\Delta t_{(min.)}$	$-\Delta P_{(mm)}$
105	3
30	2
12	2
10	2
28	2
20	2
25	2
10	2
130	16
50	5

Run No. 2 - Cumene Left Out	
$\Delta t_{(min.)}$	$-\Delta P_{(mm)}$
2	40
3	7
2	3
5	7
5	3
5	3
5	3
5	2
5	2
5	2

These points show only a representative number of the readings taken.

It was necessary to determine the products formed in the vapor phase in order to propose a mechanism which would explain the increase

in pressure. In order to make these studies, infrared spectroscopic data and vapor phase chromatograms were taken. All samples were analyzed by the vapor phase chromatograph under similar conditions for the purpose of comparison. The machine was set on a temperature of 100° C with a sensitivity of 4 and flow rate of 42.5 ml/min. The column contained DI-2-ethylhexylphthalate on 20-60 mesh firebrick and the carrier gas was helium.

The sample was tapped directly from the reaction vessel. After the pressure had increased over a period of time a polyethylene tube was extended from the left arm of the system to the vapor phase analyzer. An amount of the prepared isopropyl ether was run into the reaction vessel causing an increase in pressure and forcing the gas out of the system into the analyzer. Several samples were analyzed by this method. Two distinct peaks were recognized as the result of these analyses.

Samples of the liquid reaction mixture were also examined in the analyzer. Only one peak resulted from each of these samples.

On the basis of the resulting peaks from both the gaseous phase and the liquid phase of the reaction mixture, suggestions were made of possible products which may exist in these phases. To disprove or verify these proposals, chromatograms were done on oxygen, hydrogen, propene, methane and a methane-oxygen mixture.

Oxygen and hydrogen samples were passed through directly from the tanks. Propene was prepared by the general lab method, i.e., by the dehydration of isopropyl alcohol with sulfuric acid. The gaseous product was first passed through bromine water until the bromine solution was decolorized and the propene samples were tapped directly from the reaction

vessel to the analyzer.

Methane was prepared from the Grignard reagent, methylmagnesiumiodide, and tapped directly to the analyzer.

The methane-oxygen mixture was prepared in the following manner. The methane was prepared from the Grignard reagent and collected in liter bottles by the displacement of water. Only half of the water was displaced by methane gas and the remaining half was displaced by oxygen from the oxygen tank. The collecting bottles were then tightly capped with 2-hole rubber stoppers that had been fitted with glass tubing in both holes and connected to rubber tubes leading from each stopper. These tubes were closed with clamps.

In order to transfer the gas mixture to the VPC analyzer, one of the tubes was connected to the water faucet and the other was connected to the analyzer. The clamps were opened simultaneously to allow water to flow into the collector bottles and force the gas into the analyzer. Several samples of the mixture were analyzed.

Another sample was taken from the gaseous phase of the isopropyl-oxygen mixture of the main reaction vessel. It was forced into a gas cell by the previously described method and subjected to infrared examinations. All data which was recorded on physical measurements were compiled and evaluated.

CHAPTER V

GENERAL EVALUATION OF EXPERIMENTAL WORK

Preliminary. - It was observed that there were initial increases in pressure of several of the many systems described in the preliminary experiments. These initial increases were always resolved into pressure decreases. There were pressure increases only when cumene was omitted from the systems. This suggested that whatever compounds were being formed which caused the increase in pressure were soluble in cumene.

But unlike the continuous and standing pressure increase as was expected by proposed mechanisms with certain mixtures of isopropyl ether, benzoyl peroxide and t-butyl alcohol, there was no noticeable reaction and benzoyl peroxide did not dissolve. This implies that the reaction was possibly inhibited by the alcohol. Cumene was added to the system to increase the solubility of the benzoyl peroxide. There was still no noticeable reaction. When the system was set up without the alcohol reactions warranted the conclusion that oxygen had been absorbed by some medium in the system.

To verify or disprove this theory, oxygen-free systems were used in which there was no indication of a decrease in pressure. Systems which contained large amounts of oxygen showed a decrease in pressure. It was shown that cumene did not absorb oxygen whereas isopropyl ether did. Cobalt II chloride and chloroacetic acid inhibited the absorption of oxygen.

Additional data was needed for a more substantial conclusion that oxygen was being absorbed by the ether and not the peroxide. A search was then made for a peroxide whose structure should be readily susceptible to the absorption of oxygen. Phthaloyl peroxide was suggested for this purpose.

This compound was carefully prepared and thoroughly tested for its ability to absorb oxygen. From experimentation it was suggested that the oxygen was not absorbed by the peroxide, but rather by the ether.

The table below will give an over-all picture of the results of the preliminary investigations:

TABLE 2.--Results of preliminary experimentation

RUN NO.	SAMPLE	CHEMICALS USED	RESULTS
1	I (Blank)	20 ml $iPr)_2O$ 200 ml t-BuOH 4.6 gm Bz_2O_2	Bz_2O_2 failed to dissolve. Cumene was added to increase solubility (23.5 gm). No noticeable reac'n. Bz_2O_2 remained undissolved.
	II	20 ml $iPr)_2O$ 200 ml t-BuOH 4.6 gm Bz_2O_2 11 mg $CoCl_2$	No noticeable amt of Bz_2O_2 dissolved. Cumene was added (23.5 gm). No noticeable reac'n. Bz_2O_2 remained undissolved.
	III	20 ml $iPr)_2O$ 200 ml t-BuOH 4.6 gm Bz_2O_2 11 mg $CoCl_2$	No noticeable amt of Bz_2O_2 dissolved. Cumene (23.5 gm) was added. No noticeable reac'n. Bz_2O_2 remained undissolved.
2	I (Blank)	20 ml $iPr)_2O$ 4.6 gm Bz_2O_2 200 ml cumene	Greatest decrease in pressure. Bz_2O_2 dissolved.

TABLE 2--Continued

Run No.	Sample	Chemicals Used	Results
	II	20 ml $iPr)_2O$ 4.6 gm Bz_2O_2 11 mg $CoCl_2$	Decrease in pressure about 1/3 that of reac'n vessel I. Bz_2O_2 dissolved. $CoCl_2$ remained undissolved.
	III	20 ml $iPr)_2O$ 4.6 gm Bz_2O_2 11 mg $CoCl_2$ 11 mg ClHOAc 200 ml cumene	Little or no change. Bz_2O_2 dissolved. $CoCl_2$ remained undissolved.
3	I (Blank)	20 ml $iPr)_2O$ 200 ml cumene Bz_2O_2 catalyst O_2 flushed	Decrease in pressure to same extent as reac'n vessel I in trial 2 above.
	II	20 ml $iPr)_2O$ 200 ml cumene Bz_2O_2 catalyst N_2 flushed	No change.
4	I	20 ml $iPr)_2O$ 200 ml cumene O_2 flushed	No noticeable change.
	II	30 ml $iPr)_2O$ O_2 flushed	Increase in pressure immediately.
	III	30 ml cumene O_2 flushed	No noticeable change.
5	I	20 ml $iPr)_2O$ 200 ml cumene Bz_2O_2 catalyst O_2 flushed	Decrease in pressure.

TABLE 2--Continued

Run No.	Sample	Chemicals Used	Results
	II	40 ml $iPr)_2O$ few drops iPrOH Metallic Na O_2 flushed	Immediate increase in pressure. When checked later, pressure had decreased.
6	I	40 ml $iPr)_2O$ $CoCl_2$ catalyst O_2 flushed	Immediate increase in pressure after swirling of vessel but began to decrease.
	II	$iPr)_2O$ ClHOAc O_2 flushed	Increase in pressure but not as rapidly as in sample I and to a smaller extent.

Major. - An over-all evaluation of the kinetic data was made with respect to the products formed. Comparisons of the resulting peaks were made of all samples. It was concluded that none really coincided to the extent that an identification of products might be made. It is noted that two peaks were the results of the gas which caused the increase in pressure in the reaction vessel containing the purified isopropyl ether-oxygen mixture. It was suggested that the gas phase products were methane and oxygen. After testing a mixture of the two gases, it was observed that the analyzer did not separate the two gases and only one peak was realized. This eliminated the proposed methane-oxygen mixture.

Neither oxygen, isopropyl ether, propene, methane or hydrogen chromatograms was in accord with the peaks that resulted from the gas phase mixture of the main reaction vessel. Thus, all suggested possibilities were held for further investigation.

The infrared data gave little insight into the unsolved problem of compounds formed. This too warranted additional data.

Without some indication as to what compounds were present in both phases of the reaction, i.e., the reaction which is responsible for the pressure increase and that which is accredited for the pressure decrease, there is very little conclusion that can be made about the reaction.

However, it was suggested that the pressure increase is probably due to a unimolecular photoinitiated oxidation to the peroxide:

$$RH + O_2 \longrightarrow ROOH$$

where RH represents the isopropyl ether. This reaction is followed by a light catalyzed decomposition of the hydroperoxide:

$$ROOH \longrightarrow RO\cdot + \cdot OH$$

The over-all equation being

$$RH + O_2 \longrightarrow RO\cdot + \cdot OH$$

With the vapor pressure of the RH remaining constant at the temperature of the reaction only the oxygen pressure would be taken into consideration.

Another suggested possibility was that the reaction followed a bimolecular pressure increase process:

$$2\ RH + O_2 \longrightarrow 2\ ROOH$$

$$2\ ROOH \longrightarrow RO\cdot + H_2O + \cdot OH$$

The over-all equation for this process would be

$$2\ RH + O_2 \longrightarrow RO\cdot + H_2O + \cdot OH$$

From inspection of these equations it is indicated that an increase in pressure is realized in either case.

The decrease in pressure is due to an ultimate absorption of oxygen by a medium in the system. On the basis of experimentation and elimination, it has been concluded that this medium is isopropyl ether. In order to determine the rate of this absorption, further study is required.

CHAPTER VI

SUMMARY AND CONCLUSION

It has been indicated in this paper that there is no substantial basis for making calculations related to kinetic studies or conclusions on the general study. However, much information has been gathered and compiled concerning the isopropyl ether-oxygen system at room temperature.

It has been established, however, that isopropyl ether does absorb oxygen after an immediate initial pressure increase unless cumene is present in the system. If cumene is present, there is an induction period before absorption is realized but no pressure increase.

The data contained herein will serve as background material for further investigation of the described system and it is suggested that before conclusions are made said study should be carried out.

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